URBAN TREES AS SINKS FOR SOOT: DEPOSITION OF ATMOSPHERIC ELEMENTAL CARBON TO OAK CANOPIES AND LITTERFALL FLUX TO SOIL

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Elemental carbon (EC), a product of incomplete combustion of fossil fuels and biomass, contributes to climate warming and poor air quality. In urban areas, diesel fuel trucks are the main source of EC emissions from mobile sources. After emission, EC is deposited to receptor surfaces via two main pathways: precipitation (wet deposition) and directly as particles (dry deposition). Urban trees may play an important role in removing EC from the atmosphere by intercepting and delivering it directly to the soil. The goal of this research was to quantify the magnitude of EC retention in leaf waxes (in-wax EC) and EC fluxes to the soil via leaf litterfall in the City of Denton, Texas. Denton is a rapidly growing urban location in the Dallas-Fort Worth metropolitan area. A foliar extraction technique was used to determine EC retention in leaf waxes. Foliar samples were collected monthly, from April through July, from pairs of Quercus stellata (post oak, n=10) and Quercus virginiana (live oak, n = 10) trees. Samples were rinsed with water and chloroform in a two-step process to determine EC retained in leaf waxes. A Sunset OC/EC aerosol analyzer was utilized to analyze the EC content of extracts filtered onto quartz-fiber filters. From April through July, leaf litter was collected bi-weekly under 35 trees (20 post oak, 15 live oak), and oven dried to determine dry weight. EC retained by tree canopies was estimated by multiplying in-wax EC by canopy leaf area index, while EC flux to soil was estimated by multiplying in-wax EC by leaf litterfall mass. This study shows that through retention of EC in leaf waxes, urban tree canopies represent important short-term sinks for soot in urban areas.

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CHAPTER 1

ELEMENTAL CARBON AND ITS DEPOSITION TO URBAN TREES AND SOILS

Introduction

Elemental carbon (EC) is a component of fine particulate matter (PM; particles 2.5 microns [µm] or smaller) emitted to the atmosphere during biomass and fossil fuel burning (Bond *et al.* 2013, Table 1). Also referred to as soot or black carbon (BC) due to its color, EC particles absorb incoming solar radiation, decreasing the amount of solar radiation reradiated back to space by emitting it as heat energy (Bond *et al.* 2013). This positive radiative forcing contributes to climate change by increasing global temperatures (Bond *et al*. 2013, Table 1).

Elemental carbon can also be detrimental to human health. Studies show that in areas with high levels of biomass and fossil fuel burning (e.g., urbanized areas) there are increased incidences of pulmonary disease and decreased cognitive function among human populations (Davidson *et al.* 2007, Suglia *et al.* 2007). An EC particle can be smaller than a red blood cell (70-500 nanometers), resulting in its ability to enter the bloodstream and cause cardiovascular disease (Nichols *et al.* 2013).

Elemental carbon's contribution to climate change as well as its threat to human health has spurred an increase in recent atmospheric research on EC, the majority focused on tracing and identifying its sources (Barrett & Sheesley 2017, Lena *et al.* 2002, Novakov *et al.* 2000). However, little is still known about pathways of EC removal from the atmosphere. Atmospheric particles are deposited to the Earth surface through two main pathways: wet and dry deposition. Particles dissolved or enveloped in precipitation define wet deposition, while those that fall to the surface only as particles or gases define dry deposition (Weathers & Ponette-

González 2011). Removal of EC particles from the atmosphere via these deposition pathways is a critical process in the delivery of EC from the atmosphere to the soil, an important EC sink. Soil in temperate regions has been found to store EC for up to 13,000 years (Gavin *et al.* 2003). Sequestration of EC is important for reducing its impacts on climate and air quality, particularly in urban areas.

While urbanized areas account for only 2% of the global land surface, they produce approximately 78% of its carbon emissions (O'Meara 1999). Elemental carbon is especially abundant in urban atmospheres, where it is emitted from sources such as diesel fuel trucks and coal-fired electricity plants (Zhu *et al.* 2002). One strategy to enhance atmospheric EC removal and increase EC sequestration in urban ecosystems is to enhance tree cover (Beckett *et al.* 2000a, Beckett *et al.* 2000b, Grote *et al.* 2016, Janhäll 2015, Nowak *et al.* 2006).

In this introductory chapter I review elemental carbon, the hazards of urban air pollution, mechanisms of PM removal from the atmosphere, the modeled quantities of PM removed from the atmosphere by urban trees, and factors that influence particulate matter scrubbing by vegetation.

Elemental Carbon: A Contributor to Climate Change

Elemental carbon has unique properties that make it an especially important contributor to climate change (Bond *et al.* 2013). It is composed of small carbonaceous spheres (Bond *et al.* 2013) and displays a bimodal distribution with peaks at 0.1 and 1 µm in urban areas (Masiello 2004). Each EC particle heats the surrounding air as it absorbs radiation, causing EC to have a larger estimated climate forcing capability than methane (+0.77 W/m^2 and 0.48 W/m^2, respectively; Bond *et al.* 2013). In fact, it is considered to be the second most important climate-forcing agent after carbon dioxide (Bond *et al.* 2013). Its light absorption capabilities can also increase when it is emitted into the atmosphere due to its mixing with other aerosol components (Bond *et al.* 2013). Elemental carbon is also insoluble in organic solvents and water (Bond *et al.* 2013), indicating that it is not easily removed from the atmosphere when freshly emitted. However, upon mixing with other aerosols, EC may become less hydrophobic. Unlike the greenhouse gas carbon dioxide, another unique property of EC is its relatively short atmospheric lifetime (Bond *et al.* 2013), indicating that it may be most effective to focus on removal of EC from the atmosphere to mitigate climate change (Grieshop *et al* 2009).

Elemental Carbon: A Component of Urban Air Pollution

In 2016, the World Health Organization (WHO) estimated that 92% of the world's population lived in areas where air quality levels exceed those set by WHO (WHO 2016). Many of these polluted areas are considered "urban areas", defined as encompassing at least 2,500 people (USCB 2015). Urban areas often produce air pollution from anthropogenic sources (e.g. factories, transportation, agriculture), and are frequently studied due to the negative health effects of pollution on humans. Anthropogenic air pollutants include those known as "criteria air pollutants" (ozone, carbon monoxide, nitrogen oxides, sulfur oxides, lead, PM_{10}, and $PM_{2.5}$), and are all damaging to the environment and human health in high concentrations over extended periods of time (EPA 2018). Although the EPA and the WHO set standards for these pollutants, many urban areas exceed these standards. One of these air pollutants that can be dangerous if exceeded is fine PM ($PM_{2.5}$), a component of which is EC.

Fine PM is an important contributor to air pollution and is often studied in relation to epidemiology due to its ability to enter the lungs and bloodstream and cause respiratory and cardiovascular diseases (Brook *et al.* 2010, Goldberg *et al.* 2001, Koenig *et al.* 1993, Pope *et al.* 2002, Pope & Dockery 2006). Although fine PM exists in non-urban areas, it is also created and dispersed anthropogenically from sources such as vehicular movement causing fugitive dust, as well as factory production (EPA 2018, Table 1).

It is important to study methods of mitigation for fine PM in urban areas where the population is high, producing more pollution and a higher number of negative health effect instances. In addition to health effects, fine PM can also cause environmental concerns. These concerns include corrosion due to dry particle acid rain deposition, and the creation of haze and visibility issues from light reflection off of particles (EPA 2018). Because EC is a component of fine PM, all concerns mentioned above apply to it. It has been shown to cause human health issues (Nichols *et al.* 2013), as well as atmospheric warming (Bond *et al.* 2013). As a contributor to urban air pollution, it is important to study EC and its deposition from urban atmospheres for the sake of human health and the environment.

Atmospheric Particulate Matter Deposition

To date, EC has been quantified more frequently in the atmosphere than in deposition. For example, Lena *et al.* (2002) studied atmospheric EC concentration in relation to truck traffic and found that EC along truck routes was almost 3-fold greater than at background sites. Source apportionment studies have also been conducted in which researchers have studied remote areas to determine if EC sources are mainly due to biomass burning or fossil fuel combustion (Barrett & Sheesley 2017, Novakov *et al.* 2000). Takahama *et al.* (2013) also found that EC mass concentrations can differ based on source type. Although these and many other studies assess spatial patterns and sources of atmospheric EC, more information on deposition of EC from the atmosphere is currently needed, especially in urban areas.

Atmospheric Deposition Pathways

After being emitted from sources, particles can be removed from the atmosphere and deposited onto surfaces via wet deposition and dry deposition (Weathers & Ponette-González 2011). Upon wet deposition, particles can be enveloped in precipitation particles in clouds and fall to the surface in a process known as rainout. When particles are enveloped in already falling precipitation, the process is known as washout. Through dry deposition, particles are removed from the atmosphere by gravity or direct impact with other surfaces (Beckett *et al.* 2000a; Figure 1). Deposition of particles tends to decrease with distance from emission sources (Weathers & Ponette-González 2011). In addition, climate determines the amount of wet and dry deposition to surfaces (Lang *et al.* 2002, Weathers & Ponette-González 2011). Large quantities of precipitation in a climatic region increases wet deposition, while small amounts of precipitation favor dry deposition to surfaces, such as trees. In the case of topography, rates of particle deposition tend to increase with increasing elevation due to not only higher wind speeds and fog immersion, but also to orographic precipitation (Ponette-González *et al.* 2016, Table 1). Another control on deposition of particles in a given area is the presence of vegetation canopies, which possess important characteristics for particle capture from the atmosphere (Ponette-González *et al.* 2016).

Atmospheric Particulate Matter Deposition to Tree Canopies

Research shows that trees possess certain characteristics that encourage pollutant deposition (Grote *et al.* 2016). At the canopy scale, trees have a more complex structure than shrubs (Beckett *et al*. 2000a) and other urban materials (e.g., glass, concrete), promoting particle capture (Beckett *et al.* 2000a). In addition to their tall stature, trees have a large Leaf Area Index (LAI), high surface roughness, and the ability to generate turbulence which encourages particles to mix deeper into tree canopies than into vegetation with smooth surfaces (Ponette-González *et al.* 2016, Table 1). Trees with larger leaf area accumulate more particles than those with smaller leaf area. For example, evergreen coniferous trees are more efficient than deciduous broadleaved trees at capturing particles due to their larger LAI and because conifers retain their needles year round (Weathers *et al.* 2006). Temporally, leaf abscission from deciduous tree species occurs in late autumn; thus, most leaf capture of particles will occur in the months prior to abscission as well as after regrowth (Hara *et al.* 2014, Table 1).

At the leaf scale, multiple studies show that trees with trichomes (hair-like outgrowths) on their leaves display increased particle interception when compared to leaves with fewer trichomes (Chen *et al.* 2017, Jamil *et al.* 2009, Mo *et al.* 2015, Saebø *et al.* 2012, Weber *et al*. 2014). Saebø *et al*. (2012) determined that thicker epicuticular waxes allow for a higher capture rate of small particles than those with thinner waxes. In fact, only particles smaller than 10 microns are usually retained in leaf waxes (Terzaghi *et al*. 2013), and EC particles tend to be less than 2.5 microns. Saeboø et al. (2012) found that although conifer leaves lack rough or hair-covered surfaces, broad-leaved trees have a larger boundary layer and therefore are not as efficient at capturing particles (Table 1). Table 2 shows a brief summary of publications involving experimental studies of air pollution capture by and retention in vegetation.

Spatial Variability in Particulate Matter Deposition to Urban Tree Canopies

Particle deposition to trees is not only driven by characteristics of the trees themselves, but also by spatial aspects. Factors that influence spatial patterns of atmospheric PM deposition to urban tree canopies include proximity to emission sources, local scale spatial distribution of trees, and wind movement and speed (Janhäll 2015, Nowak 2014, Pugh *et al.* 2012, Weathers & Ponette-González 2011, Weber *et al.* 2014).

A major factor affecting PM deposition is proximity to emission sources (Janhäll 2015, Weathers & Ponette-González 2011). Weber *et al.* (2014) found that the amount of PM deposited to vegetation is positively correlated with proximity to roads due to the fact that diesel trucks are significant pollution sources. Pugh *et al.* (2012) demonstrated the importance of placing vegetation near PM sources by calculating deposition in a modeled study. Nowak (2014) also stated that it is beneficial to use vegetation as a barrier between roads and people to act as a shield from high concentrations of PM, and it is known that the shape of vegetation barriers is important for particle deposition (Brantley *et al.* 2014).

Wind speed and particle size play roles in deposition to tree leaves. The faster a particle is moving, and the smaller the particle, the more likely it is to embed into the epicuticular waxes of leaves (Dzierźanowski *et al.* 2011). In modeled studies using wind tunnels, air is forced directly through the tree canopy being tested; however in ambient conditions, the 'street canyon effect' creates a wind vortex in which particles in air can pass above or even around the sample tree (Janhäll 2012). In addition, tree cover can reduce local sources of fine PM from wind-borne soil by decreasing wind speeds (Nowak 2014).

Quantities of Particulate Matter Removal by Urban Forests

Few studies have measured PM removal on an urban city scale, yet research indicates that urban trees can capture considerable amounts of PM (Nowak *et al.* 2006, Yang *et al.* 2005). A 3-year study conducted by McPherson *et al.* (1994) in the urban forest of Chicago showed an estimated 234 tons of PM removed by trees in the year 1991. In the City of Beijing, China, a study of an urban forest model made up of multiple native trees estimated an annual removal of PM less than 10 microns totaling 772 tons (Yang *et al.* 2005). Nowak *et al.* (2006) conducted a meteorological modeling study to detect the amount of gaseous and particulate air pollution removed by urban forests across the coterminous United States. This study resulted in a total of approximately 711,000 metric tons of pollutants removed annually, with up to 3.5% of PM removed in individual cities. McDonald *et al.* (2007) conducted a study in the UK in two separate conurbations using GIS analysis. When tree cover was increased from 3.7% to 16.5%, PM concentrations decreased in the West Midlands conurbation by 10%. In the Glasgow conurbation, PM concentrations decreased by 2% when urban forestry was increased from 3.6% to 8%. While each of these studies demonstrates that PM can be removed from the atmosphere by urban tree filtration, they are lacking in a focus on sequestration of PM (in particular, EC) and are mostly based on modeling instead of measurements.

Urban Litterfall

After deposition to canopies, particles can be delivered to the soil via two pathways: throughfall and litterfall. Throughfall is defined by precipitation falling through tree canopies, and litterfall is any organic matter that falls to the ground from the trees. Litterfall has the potential to be a significant pathway for EC delivery to the soil in areas dominated by deciduous trees, but rarely has it been quantified. Hara *et al*. (2014) estimated BC deposition in litterfall in a suburban forest in Japan. Multiple trees were sampled to determine BC retention on leaves, with leaf samples taken at different heights of individual trees. Monthly litterfall was collected and dried. They found a large flux of litterfall to the ground in the month of September, with the BC mass of litterfall at over 5 mg/m^2. The smallest amounts of BC mass of litterfall were in the months of April, May, and June, each totaling averaging approximately 0.2 mg/m^2. Litterfall under individual, urban trees is not well studied, and the majority of published literature on litterfall is outdated.

Conclusion

Although research on urban tree capture of PM is becoming more common, there are still large gaps in knowledge about EC and its deposition to urban trees. Preservation and planting of trees in urban areas are likely important factors in densely populated areas, as it will become more important than ever to combat climate change and human health hazards through the use of effective urban form. This thesis provides a component of that research by quantifying EC captured in leaf waxes, as well as EC that is delivered to the ground in litterfall.

CHAPTER 2

URBAN TREES AS SINKS FOR SOOT: DEPOSITION OF ATMOSPHERIC ELEMENTAL CARBON TO OAK CANOPIES AND LITTERFALL FLUX TO SOIL

Introduction

Particulate matter (PM) air pollution - a product of incomplete combustion (e.g. fuel burning) and non-combustion (e.g. fugitive dust) sources - has been shown to be hazardous to human health and the environment, especially in highly populated urban areas (Cohen *et al.* 2004). Studies show that inhalation of PM can cause cardiovascular (Brook *et al.* 2010, Goldberg *et al.* 2001) and pulmonary complications (Koenig *et al.* 1993), and urban area PM has been associated with mortality (Laden *et al.* 2000, Mar *et al.* 2000, Schwartz *et al.* 2002). Particulate matter is often separated into two categories: coarse PM, particles with diameters larger than 2.5 and smaller than 10 micrometers (e.g. dust, seasalt), and fine PM, particles 2.5 micrometers or smaller (e.g. sulfates, nitrates, carbon).

One component of fine PM is elemental carbon (EC), often known as black carbon. Elemental carbon is made up of small carbonaceous spheres, and is emitted into the atmosphere primarily from fossil fuel combustion and biomass burning (Bond *et al.* 2013). The largest global source of EC is grassland and forest burning, but in urban areas the main source of EC is diesel fuel exhaust (Bond *et al.* 2013). When it is emitted into the atmosphere from diesel engines, such as those used for the transportation of goods, EC strongly absorbs incoming solar radiation, and absorption can be enhanced upon EC mixing with other aerosols (Bond *et al.* 2013). Elemental carbon has a larger estimated climate forcing capability than methane (+0.77 W/m^2 and 0.48 W/m^2, respectively; Bond *et al.* 2013). Given its effects on human health and climate, it is important to remove EC from the atmosphere, particularly in densely populated areas.

Numerous studies highlight the role of trees and other vegetation in capturing PM from urban atmospheres (Beckett *et al.* 2000a, Brantley *et al.* 2014, Branquinho *et al.* 2008, Burkhardt & Grantz 2017, Cai *et al.* 2017, Chen *et al.* 2017, Dzierżanowski *et al.* 2011, Freer-Smith 2004, Mo *et al.* 2015, Mori *et al*. 2015, Nowak *et al*. 2006, Popek *et al.* 2013, Przybysz *et al.* 2014, Reinap *et al.* 2009, Saebø *et al.* 2012, Sgrigna *et al.* 2015, Wang *et al.* 2015). Few studies, however, have focused specifically on EC removal by vegetation (Hara *et al.* 2014). Both coarse and fine particles, including EC, can be deposited onto leaf surfaces through wet or dry deposition (Weathers & Ponette-González 2011). Wet particulate deposition occurs when particles are incorporated into precipitation (rainout) or when particles collide with raindrops as they fall (washout). Particles can be also dry-deposit directly onto leaves (Ponette-González *et al.* 2016). Wind speed influences dry deposition of particles, as do the shape and structure of leaves, and the amount of trichomes on the surface of the leaves (Ponette-González *et al.* 2016, Ponette-González *et al.* 2016). In addition to residing on leaf surfaces, PM can also embed within leaf waxes (Dzierżanowski *et al.* 2011, Mo *et al.* 2015, Saebø *et al.* 2012, Sgrigna *et al.* 2015). There is some evidence that coarse particles are preferentially deposited to leaf surfaces whereas fine particles are preferentially retained within leaf waxes (Dzierżanowski *et al.* 2011).

In general, trees have a higher capacity to capture and retain particles compared to shrubbery (Cai *et al.* 2017, Chen *et al.* 2017, Mo *et al.* 2015, Saebø *et al.* 2012). Weathers *et al.* (2006) found that LAI is positively correlated with PM deposition, indicating that more PM will be deposited into trees, which have a larger LAI than shrubs (Cai *et al.* 2017). In addition, shrubs tend to be nearer to the ground than trees, indicating that trees can intercept particles before they reach shrubs (Mo *et al.* 2015). In growing urban areas, trees are often cleared for development. Because trees are effective "air filters", it is important to understand and quantify the amount of EC that can be retained by tree canopies.

It is not only important for EC to be removed from the atmosphere, but also for it to be sequestered in areas not harmful to humans or the environment. Aside from the canopy, another potential long-term sink, or storage place, for EC is the soil. In vegetated ecosystems, leaf litterfall is a major pathway by which nutrients and pollutants are delivered from aboveground vegetation to the soil (Vitousek 1984). Because PM can be retained in leaves and potentially enter the soil after leaf degradation, it is possible that EC can eventually be incorporated into the soil for long-term storage.

Research Objectives

This study aims to understand and quantify EC retention in the waxes of two urban, broad-leaf tree species. The objectives of this research are twofold: (1) quantify spatial and temporal variability in leaf- and canopy-scale EC retention by urban oak trees; and (2) determine the magnitude of litterfall and in-wax EC fluxes in leaf litterfall to below-canopy soils.

Study Area

Population Growth and Air Quality

This study was conducted in the City of Denton (33.2148°N, 97.1331°W), Texas, located within the Dallas-Fort Worth (DFW) Metropolitan Area. The City of Denton is part of one of the fastest growing counties in the U.S. (U.S. Census Bureau 2016). From April 2010 to July 2016, Denton County saw an estimated 21.1% population increase (U.S. Census Bureau 2016). Although the City of Denton has a much smaller population (133,808 people as of July 2016) than the cities of Fort Worth (854,113 people) and Dallas (1,317,929 people), air pollution is a concern. The Texas Commission on Environmental Quality monitors nitrogen oxides (NO_x), ozone (O_3), and particulate matter concentration <2.5 µm (micrometer) in diameter ($PM_{2.5}$) at Denton Airport South Continuous Ambient Monitoring Station (CAMS 56; 2017). Between 2014-2016, Denton's maximum 8-hour average ground level ozone concentrations were the highest in the State of Texas. During these years, the City of Denton experienced a maximum eight-hour average of 80 parts per billion (ppb) of ozone (TCEQ 2017), exceeding the National Ambient Air Quality Standard (NAAQS) eight-hour average of 70 ppb (EPA 2016). The primary NAAQS for $PM_{2.5}$ is a one-year average of 12.0 µg/m^2, averaged over three years. For the year of 2016, Denton's average $PM_{2.5}$ level was 7.6 µg/m^2 (TCEQ 2017).

Rainfall and Temperature

The City of Denton has a variable climate due to its subtropical location. The 30-year normal or average measured at Denton Enterprise Airport (KDTO) is 967.49 ± 25.17 millimeters (mm). During this study, from April to July 2017, rainfall totaled 411.99 mm, slightly higher than the 30-year normal of 364.24 mm for the same month range. The City of Denton also experiences periods of heavy and intense rainfall; the total rainfall for a single event in 2017 was nearly 76.2 mm. Heavy rainfall is frequently followed by extended periods of little to no precipitation (NWS 2017) during which particulate matter can accumulate on canopy surfaces.

In the City of Denton, temperature varies over the course of the year. Summer temperatures during the day often reach above 37.8°C and only drop to 26.7°C in the evenings, and winter temperatures often range from highs near 13.3°C to lows near 0.6°C (NWS 2017).

Urban Forest and Focal Tree Species

According to the 2016 State of Denton Urban Forest report (State of Denton Urban Forest 2016), the City of Denton has approximately 3.5 million trees, which cover almost 30% of the city's area. City trees are predominantly found in the northeast, southeast, and southwest quadrants, determined using GIS technology.

The focal species in this study are post oak (*Quercus stellata)* and live oak (*Quercus virginiana*). Post oaks have a broad geographical distribution; they are native to Texas and can be found as far west as central Texas, as far south as mid-Florida, and as far north as Massachusetts (Stein 2003). Post oak trees are deciduous and drought-resistant, and grow on poorly formed, dry soil types (Holmes 2015). Adult post oak trees reach maximum heights of 15-25 m and form dense and rounded crowns (Stein 2003). Their leaves have two distinct sides: the shiny, dark green and roughly textured adaxial (topside) surface is opposite the light green and trichome-covered abaxial (underside) surface (Stein 2003). Studies on PM deposition to this particular species have not been conducted, but research on leaves with diverse characteristics shows that trichomes enhance particle capture (Beckett *et al.* 2000b). Post oaks grow new leaves in March and early April, with trees reaching maximum leaf area in late spring and early summer. In November and December, post oak trees shed most of their leaves with remaining leaves falling in March and early April prior to bud break (Johnson & Risser 1974).

In the City of Denton, post oaks are the third most common tree species, making up approximately 9% of the 10 most common trees in the city (State of Denton Urban Forest 2016). However, post oaks have been shown to be difficult to transplant due to their sensitivity to soil conditions and are not grown in nurseries (Russell 2009). Thus, they are not ideal species for planting programs, but rather for conservation programs.

Live oak (*Quercus virginiana*) is an evergreen species that, while not native to North Texas, is widely planted in residential yards and urban greenspaces. It is found in warm-temperate climates from Virginia to the southern end of Florida (Goldman 2016), and is very drought tolerant (Qi *et al.* 2006). Live oak trees reach maximum heights of 15-25 m, and can grow a very large crown up to 45 m wide (Goldman 2016). Live oak leaves are much smaller than post oak leaves, and their structure varies depending on whether they are exposed to shade or sun. Sun-grown leaves develop similarly to those of post oaks, with thick, shiny adaxial surfaces and trichome-covered abaxial surfaces (Qi *et al.* 2006). Shaded leaves do not develop trichomes on their green abaxial surfaces (Goldman 2016). Live oaks flower and their leaves drop and regrow in early spring (Goldman 2016, Qi *et al.* 2006). Although post oak trees in the City of Denton are more widespread than live oak trees (State of the Denton Urban Forest 2016), live oaks are excellent for reforestation projects in North Texas due to their drought tolerance and their deep root structures (Qi *et al.* 2006).

While both post and live oak trees appear to have a high potential for particle capture based on their leaf and crown structures, there are potential downfalls of using oak trees for particle air quality mitigation. The *Quercus* genus emits higher levels of volatile organic compounds (VOCs) compared to other genera (Table 1). According to a study by Nowak *et al.*

(2002), *Quercus* and *Platanus* species emitted 42% of total VOCs in Brooklyn's urban forest. However, that study also found that the urban forest removed a total of 0.25% of airborne particulate matter hourly. Tradeoffs between VOC emissions and particulate carbon capture have yet to be assessed.

Materials and Methods

Tree Selection and Vegetation Measurements

To assess the role of vegetation canopies as a short-term sink for EC, and to understand the amount of EC retention in waxes over time, we quantified EC retention in leaf waxes. Twenty trees (10 post oaks and 10 live oaks) were selected for foliar sampling across the City of Denton (Figure 2a, Table 3). Post oak and live oak trees were chosen based on accessibility as well as proximity to roads (near roads ≤ 100 m, far from roads > 100 m) and to one another (Table 4). Six pairs of trees were co-located (≤200 m apart), while four pairs were not co-located but sampled in similar settings (i.e., near or far from road).

A Trimble Geo 5T handheld Global Positioning System (≤1 m ± resolution, Trimble, Inc., Sunnyvale, CA) was used to map the location of each tree (Table 3). Diameter at breast height (dbh, 1.3 m aboveground) and height of each tree were measured using a Forestry Suppliers Inc. English Steel dbh tape (Model 343D, Jackson, MS) and a TruPulse Rangefinder 360 (Laser Technology, Inc., Centennial, CO) respectively. A LAI-2200 Plant Canopy Analyzer (LI-COR, Inc., Lincoln, NE) was employed to measure tree leaf area index (LAI, one-sided foliage area per ground surface area, m^2/m^2). Pre-dawn measurements were conducted underneath each tree, approximately halfway between the outer edge of the crown and the tree bole. Four measurements were taken under each tree: the first on the south side of the tree, then moving clockwise at each of the other three cardinal directions. The average of these four measurements was used to calculate the LAI of each sample tree.

On average, post oaks had a slightly larger dbh, similar height, and smaller LAI than live oaks (Table 3). The dbh of post oaks ranged from 44.5 to 88.0 cm (mean 61.3 ± 5.1 cm), height ranged from 10.4 to 16.0 m (mean 12.8 ± 0.6 m), and LAI ranged from 1.8 to 3.6 m^2/m^2 (mean 2.4 ± 0.2 m^2/m^2). For live oaks, dbh ranged from 32.0 to 79.0 cm (mean 54.0 ± 5.3 cm), height ranged from 9.0 to 16.5 m (mean 11.5 ± 0.7 m), and LAI ranged from 2.3 to 4.8 m^2/m^2 (mean 3.4 ± 0.2 m^2/m^2).

Foliar Sampling

Foliar sampling was conducted at the beginning of each month from April through July, for a total of four sampling periods. During each sampling period, a Notch Equipment Big Shot® line-launcher was used to remove small clusters of leaves from three locations on the outer surface of the crown. Leaves were sampled from the south-facing side of each tree between 135-225 degrees, due to the direction of prevailing winds. Leaves were collected from mid-canopy, between 7-12 m aboveground depending on actual tree height. This height range was selected because the middle portion of the canopy is generally where leaf area is greatest (Owens 1996). In addition, EC particles emitted in urban areas are likely deposited to canopy surfaces from above and below due to on-road emissions.

Foliar Extraction and Analysis

After collection, leaf samples were transported to the Ecosystem Geography Laboratory at the University of North Texas (UNT) in brown paper bags, where EC particle retention on leaf surfaces was determined using a two-step foliar extraction technique after Dzierźanowski *et al*. (2011) and Hara *et al.* (2014). Leaves were immediately clipped from the branches and 10 post oak leaves and 16 live oak leaves were used in the extraction process. This number of leaves was selected to ensure sufficient surface area for particle capture. Leaves were chosen based on their health; leaves with dead areas or affected by herbivory were not selected.

Leaves were placed in a 1000 mL glass beaker and rinsed in 250 mL of double-deionized (DDI) water for 60 seconds to remove 'rain-washable' EC particles. Leaves were then removed from the water and placed in open bags to air-dry overnight. To increase EC recovery from rinse water (Torres *et al.* 2014), 1.5 g of ammonium dihydrogen phosphate ($(NH_4)H_2PO_4$) per 100 mL of water were then added to each rinse water sample. The 250 mL samples were sonicated in a HealthSonics Ultrasonic Cleaner T3.3C (HealthSonics, Algonquin, IL) for 15 minutes and poured into a 500 mL amber bottle for storage overnight. The following day, the front and back of all air-dried leaves were scanned. The open source software ImageJ (Ferreira & Rasband 2011) was used to measure the adaxial and abaxial surface areas of each leaf and average surface area per leaf calculated. Rinse water samples were then filtered through an Advantec 13-mm filter funnel into a Buchner flask over a 13-mm^2 punch of Pall quartz-fiber filter (Pall Corp., Washington, NY). Rinse water filters were stored for future analysis.

Subsequently, each sample of leaves was rinsed with 150 mL of chloroform to dissolve the epicuticular wax layer and extract EC particles retained in leaf waxes ('in-wax' EC).

Chloroform extracts were filtered using the same process as the rinse water samples. All filters were placed in individual clean petri dishes, desiccated overnight, and stored in a freezer until analysis could be performed.

Filters were transported to Baylor University where they were analyzed in the Sheesley Laboratory using a Sunset Organic Carbon/Elemental Carbon (OC/EC) Aerosol Analyzer (Sunset Laboratories, Inc., Tigard, OR). For quality assurance, sucrose spike samples of 5-57 µg of carbon were run after turning on the instrument to ensure calibration, and triplicate tests of background site air samples from Riesel, Texas were run after every 10 samples. To determine recovery of the extraction method, two, four, six, and eight µg of fullerene soot (a proxy for EC, Thermo Fisher Scientific, Waltham, MA) were added to 200 ml of water each, then filtered using the same process. Fullerene soot recovery averaged 84.4%, ranging from 95% (2 µg of EC) to 73.9 % (8 µg of EC), and a limit of detection for the instrument was determined to be 0.23 µg of carbon per cm^2 of filter (Birch & Cary 1996).

Litterfall Sampling

Twenty post oak and 15 live oak trees were selected for litterfall sampling across the City of Denton (Figure 2b). Most sites were selected in residential areas where traps were less likely to be disturbed or stolen. Litterfall traps were constructed following the National Atmospheric Deposition Program (NADP) Litterfall Mercury Monitoring Initiative protocol (NADP 2012). Each litterfall trap consisted of a 33.02-cm^2 plastic box (Farmplast, LLC, Parsippany, NJ) with 27.94-cm walls on each side. Fiberglass screenware mesh 2-mm thick (Saint-Gobain, Malvern, PA) lined the bottom and sides of the box to allow water drainage.

Samplers were placed approximately halfway between the base of the tree and the outer canopy, on the south side of the tree at an angle between 135-225 degrees. Samples were collected biweekly (every two weeks) from 2 April 2017 to 23 July 2017. Samples were placed in bags, transported to the Ecosystem Geography Laboratory at UNT, and sorted into leafy and non-leafy (e.g. twigs, seeds) categories. Samples were oven dried in a Thermo Scientific Heratherm Advanced Protocol oven (Thermo Fisher Scientific, Waltham, MA) at 65°C for two days, then weighed to the nearest hundredth, and sample weight (g) was recorded.

Leaf Observations

In addition to foliar and litterfall sampling, individual leaves were removed from the outer crown on the south side of post and live oaks and were qualitatively observed for trichome and epicuticular wax density. The adaxial and abaxial surfaces of three leaves from a sample post oak (PO0225) and three leaves from a sample live oak (LO0225) were observed using a Nikon SMZ660 light microscope (Nikon Instruments, Melville, NY) in the Dickstein Laboratory. Additionally, during chloroform extractions, the extent of wax buildup on the inside of the 1000 mL glass beaker was observed for both species.

Calculations

Elemental carbon retention in the leaf wax of each sample tree was calculated for each of the four sampling periods. In-wax EC was calculated by dividing EC mass measured on each filter by the total leaf surface area extracted with chloroform, resulting in EC mass per unit leaf area (μg/cm^2), which was converted to μg/m^2 for reporting. Changes in leaf-scale EC retention over time were examined by calculating net EC accumulation rate. This was calculated by dividing the amount of EC retained in leaf waxes by the cumulative number of days since post oak leaf flush on 10 March 2017 (Table 1). Net EC accumulation is reported in µg/m^2/day. Leaf-scale differences in EC retention over space were determined by computing the geometric mean of EC mass per unit leaf area for the four sampling periods for each tree. The geometric mean was used for EC content instead of the arithmetic mean because the geometric mean allowed for less sensitivity to the large outliers that occurred in April and May, therefore providing a more accurate measure of central tendency for a small, but variable dataset. When EC content is used and geometric mean is reported, it is accompanied by a standard deviation. When EC content is not included in a calculation and arithmetic mean is reported, it is accompanied by a standard error. To calculate canopy-scale EC retention, EC mass per unit leaf area (µg/m^2) was multiplied by tree LAI (m^2/ m^2) for both post and live oaks, resulting in EC mass per unit canopy area (µg/m^2).

To calculate the mass of EC deposited to soil via leaf litterfall, bi-weekly samples of leafy mass were first summed for each sample tree and month sampled. Because mass of leaf litterfall was determined in grams, and EC mass in per unit surface area (µg/cm^2), simple linear regression was used to determine the relationship between leaf weight and leaf surface area for each species. A total of 200 leaves (100 post oak and 100 live oak) were collected from the 20 sample trees across the City of Denton in August of 2017. Leaves were scanned, measured for leaf surface area using ImageJ, dried at 65°C, and then weighed. Using these data, simple linear regressions between leaf dry weight and leaf surface area were determined for each species. Both variables were log-transformed to meet assumptions of normality. Using the regression equations calculated for each focal species (for post oaks: Log_{10}[Average leaf surface area (cm^2)] = 1.7915862 + 0.8834698*Log_{10}[Leaf dry weight (g)], R^2 = 0.87; for live oaks: Log_{10}[Average leaf surface area (cm^2)] = 1.76928 + 0.995723*Log_{10}[Leaf dry weight (g)], R^2 = 0.87), leaf dry mass (g) was then converted to leaf surface area (cm^2). The data were then back-transformed to attain the surface area of leaves in each litterfall trap per month. The geometric mean of in-wax EC for each species and month was then multiplied by litterfall surface area to obtain EC in litterfall in μg/m^2/month.

Statistical Analysis

All variables (in-wax EC retention at both leaf and canopy scale, net accumulation of in-wax EC over time, tree distance from roads, litterfall flux, and EC in leaf litterfall flux) were tested for normality using the Shapiro-Wilk W goodness of fit test. Where variables did not fit a normal distribution, they were log-transformed, and where the transformations did not result in a normal distribution, non-parametric tests were used. The non-parametric Friedman test was used to examine differences in in-wax EC content between species and months. To examine accumulation rate over time, multiple linear regression was used with in-wax EC accumulation rate (μg/m^2/day) as the dependent variable, and species and month as independent variables. For litterfall, a log transformation was used to normalize the data. Leaf and non-leaf litterfall were used separately as dependent variables against the independent variables of month and species in a two-way ANOVA. Significance for all tests was set at $p<0.05$. All calculations and statistical analyses were performed using JMPv13.

Results

In-Wax EC Retention

Post oak trees displayed consistently higher leaf-scale in-wax EC than live oak trees (Figure 3). Species differences were significant (p<0.0001), but differences among months were not. Depending on the sampling period, mean EC retention in post oak leaves was three to eight times higher than that in live oak leaves. Moreover, in-wax EC content was more variable for post oak than for live oak leaves. From April to July, the mean post oak in-wax leaf EC content ranged from 536.1 ± 247.5 to 1163.9 ± 5649.8 μg/m^2 while the mean live oak in-wax leaf EC content ranged from 138.6 ± 1739.9 to 158.3 ± 105.5 μg/m^2. Evidence of these species differences was also visually apparent on sample filters (Figure 4) and consistent regardless of the distance between trees. Across all sample periods, post oak leaves displayed more than five times higher mean EC retention than live oak leaves at both co-located and non-co-located sites (Figure 5, Figure 7).

At the canopy scale, post oaks had higher potential for EC retention than live oaks (p<0.0001). Although post oaks had slightly lower LAI than live oaks (2.4 and 3.4, respectively), post oaks retained significantly more EC in their waxes per unit leaf area than live oaks. This resulted in greater mean EC retention at the canopy scale for post oaks than live oaks (1899.8 ± 9423.3 μg/m^2 and 491.8 ± 1890.2 μg/m^2, respectively).

Leaf Observations

Through use of the light microscope, qualitative observations were made regarding the density of trichomes on post oak leaves compared to live oak leaves. Both species displayed dense trichome distributions on their abaxial surfaces. However, post oaks displayed a medium distribution of trichomes on their adaixial surfaces, while live oaks displayed no trichomes on their adaxial surfaces.

Additionally, during chloroform extractions, observation of epicuticular wax buildup on the inside of the 1000 mL glass beaker revealed a continuous buildup of wax during post oak extractions, with little to no buildup during live oak extractions.

Net EC Accumulation Over Time

There was a significant decrease in net accumulation of in-wax leaf EC over time for both species (p<0.0001, p<0.0001, R^2=0.57; Figure 6), indicating a net loss of accumulated EC particles from leaf waxes. The retention of EC in post oak leaves decreased at a faster rate than did retention in live oak leaves, with the largest relative decrease occurring from April to May for both species. Between those months, mean post oak EC retention decreased approximately 63% (from an average of 42.8 ± 205.9 to 16.0 ± 92.8 μg/m^2/day), and live oak retention decreased approximately 50% (from 5.0 ± 1.9 to 2.5 ± 1.2 μg/m^2/day).

EC Retention with Distance from Sources

Trees near EC sources (i.e. bus stops, intersections) had consistently higher EC content in their leaves than those farther away from sources. However, when the geometric mean of in-wax EC (μg/m^2) was plotted in a regression against distance from nearest road (m), there was no relationship between these variables for either species (post oak R^2=0.21, p=0.1542; live oak R^2=0.28, p=0.1394).

In the case of both species, proximity to bus stops and trees near major intersections (intersections seeing more than 4,000 vehicles per day) appeared to be one of the most important factors driving high EC content (Table 5). For example, a tree near a bus stop and a major intersection displayed the highest average in-wax EC content of all post oak trees (3099.4 ± 3182.8 μg/m^2), which is four times higher than the geometric average EC content for post oaks, 800.9 ± 838.0 μg/m^2). Regarding live oak trees, a tree near a bus stop and a major intersection displayed an average EC content (436.38 ± 2851.04 μg/m^2) three times higher than the mean (148.5 ± 106.3 μg/m^2). The average in-wax EC content of post and live oaks near EC sources was over twice as large as trees located in residential parks far from major EC sources.

Litterfall Flux

From April through July, the total leaf litterfall flux to soil under post oaks was 27.8 ± 4.0 g/m^2, 44% lower than the 50.0 ± 8.1 g/m^2 measured under live oaks. With regards to non-leaf litterfall, post oaks delivered a total of 87.1 ± 7.8 g/m^2 to the ground over the four-month sampling period, whereas live oaks delivered 104.6 ± 4.3 g/m^2 over the same time period. On average, live oaks delivered more leaf litterfall to the ground than post oaks during April, May, and June, and the two species delivered approximately the same amount of non-leaf litterfall throughout all four months (Figure 8).

A two-way ANOVA for leaf litterfall showed significant differences between the species (p=0.0001), between the months (p<0.0001), and an interaction effect between species and month (p=0.0081). A two-way ANOVA for non-leaf litterfall revealed no significant differences between the species (p=0.2800), between the months (p=0.1093), and no interaction effect between species and month (p=0.3593).

Litterfall EC Flux

Although in-wax EC is present in the canopy, there was little leaf litterfall during the four sample months. Therefore, leaf EC flux to the soil is low compared to the amount of litterfall. The geometric mean monthly EC litterfall flux ranged from 9.6 ± 8.8 to 41.7 ± 70.2 µg/m^2/month for post oaks and 2.5 ± 4.7 to 12.3 ± 10.8 µg/m^2/month for live oaks. Across all sample months, post oaks delivered a geometric mean of 22.3 ± 49.8 µg/m^2/month to the ground, and live oaks delivered 6.7 ± 10.0 µg/m^2/month. Figure 9 shows the pattern of EC delivery to the soil in litterfall. Post oaks delivered significantly more EC to the ground than live oaks (p<0.001), a significant difference between the months was observed (p<0.001), and the interaction effect between species and month was also significant (p=0.0137).

Discussion

Species Exhibit Pronounced Differences in In-Wax EC Retention

In this study, leaf scale in-wax EC retention differed by more than eightfold between post oak and live oak species in a single month. Studies conducted by Chen *et al.* (2017), Mo *et al.* (2015), Neinhuis & Barthlott (1998), and Saebø *et al.* (2012) similarly found that certain species were more efficient at capturing PM than other species. For example, in a study involving the quantification of total fine PM (sum of surface and in-wax $PM_{2.5}$), a comparison of 35 plant species (11 shrubs and 24 trees) found that *Rhus typhina* (staghorn sumac) captured the most fine PM (14.28 ± 2.66 μg/cm^2), while *Fraxinus pennsylvanica* (green ash) captured the least fine PM (0.13 ± 0.08 μg/cm^2) (Mo *et al.* 2015).

Results of this study also show that leaf-scale attributes played a more important role in EC capture than canopy-scale attributes. Post oaks and live oak trees had similar height and LAI distributions, canopy characteristics that strongly influence dry deposition rates at tree scales (Griffith *et al.* 2015) but differed considerably in leaf properties.

At the leaf scale, research shows that the amount of epicuticular wax, trichome density, and leaf shape influence PM retention (Beckett *et al.* 1998, Chen *et al.* 2017, Sgrigna *et al.* 2014). Leaves with more epicuticular wax retain more $PM_{2.5}$ than those with less wax. The qualitatively larger amount of wax buildup on the sides of the glass beaker during post oak leaf extractions than during live oak leaf extractions suggests that species differences in EC retention observed in this study may be due to differences in wax content. Additionally, leaves with more trichomes on their surfaces tend to capture more PM as well (Chen *et al.* 2017, Mo *et al.* 2015, Saebø *et al.* 2012). The qualitatively observed higher trichome density on post oak leaves than live oak leaves may have contributed to the more significant quantity of in-wax EC in post oaks leaves than in live oak leaves.

Leaf shape may also play a role in PM capture (Becket *et al.* 1998, Saebø *et al.* 2012) Although needle-shaped leaves of conifers show the highest capacity for PM capture (Chen *et al.* 2017), some broadleaved species such as *Quercus variabilis* (Chinese cork oak) with an acuminate leaf shape can capture small PM more efficiently than others such as *Sophora japonica* (Japanese pagoda tree) with an ovate leaf shape. It is likely that all of these factors played a role in the contrasting levels of leaf scale EC retention observed between post oak and live oak trees.

Net In-Wax EC Accumulation Decreases Over Time

For both post oak and live oak trees, in-wax accumulation of EC decreased significantly over time (Figure 6). This could be due to physical, chemical, or biological factors (e.g. hail damage, acid rain) that result in wax degradation, and decrease the leaf's ability to accumulate EC. Once waxes are formed over the leaves, they generally do not repair or grow back if damaged (Padgett *et al.* 2009).

When exposed to rain, wind, or hail, leaf waxes have been shown to degrade (Burkhardt 2010, Shepherd & Griffiths 2006, Van Gardingen & Grace 1991). The most significant decrease in EC accumulation for both species occurred between April and June. At least 19 thunderstorms occurred in Denton during that time period, bringing a total of approximately 335.8 mm of rain (Weather Underground 2017). Denton also received hail during a number of these thunderstorm events (hail events not recorded on Weather Underground). From June through July, Denton received 71.9 mm of rain and a recorded 12 thunderstorm events. High temperatures have also been shown to desiccate particles on leaf surfaces, encouraging degradation of waxes and a decrease in tolerance to other chemical factors (Burkhardt 2010). Denton consistently displays high summer temperatures after leaf expansion in the spring. In this study, maximum temperatures were 32°C, 30°C, 36°C, and 37°C during April, May, June, and July, respectively. These high temperatures coupled with high rainfall and frequent storms during April to June could explain the decrease in quantity of epicuticular wax, and ultimately EC retention.

A study by Feng *et al.* (2014) showed that ozone visibly increases injury of conifer needle waxes, and structurally changes them. The City of Denton is currently in a non-attainment for ozone and has been for the past three years (TCEQ 2018). For the months of April through July, ozone averages in Denton were 44.7, 53.2, 47.1, and 48.8 ppb. However, during the months of April and May, 13 days occurred in which the ozone concentrations exceeded acceptable limits, with three days above unhealthy limits for sensitive groups (e.g. children, asthma sufferers, elderly). The maximum concentration of ozone in the four sample months occurred on 8 June 2017 at 80 ppb. The monthly buildup of tropospheric ozone could have played a role in decomposing the epicuticular waxes of both species. Similarly, nitric acid in rain (Bytnerowicz *et al.* 1998), as well as pathogenic activity (Serrano *et al.* 2014), can increase decomposition rate of epicuticular waxes. Grantz *et al.* (2003) also found that PM itself can have an effect on the degradation of leaf waxes, from abrasion and desiccation. A combination of many or possibly all of these factors likely played a role in the ability of leaf waxes to retain EC over time.

Leaf-Scale In-Wax EC Retention Varies Over Space

There is currently only one study available in the literature that has quantified EC in leaf waxes (Hara *et al.* 2014). In that study, 7.11 mg of EC/m^2 leaf/month were deposited to sample leaves in a Japanese forest in 2011, and 8.31 mg of EC/m^2 leaf/month were deposited to sample leaves in 2012. In micrograms, these numbers are 7110 µg of EC/m^2 leaf/month and 8310 µg/m^2 leaf/month, respectively. The numbers reported in Hara *et al.* (2014) are an order of magnitude higher compared to the levels measured in post oak and live oak leaves. The likely cause of higher numbers in the Hara study is the location: just outside the city of Tokyo, the most populated city in the world.

Particulate matter and EC retention differs not only among cities but also within cities. In this study, post oaks displayed a 8.5-fold difference in EC retention across space, and live oaks a 6-fold difference. Wang *et al.* (2015) also found differences in PM retention over space, in which trees nearer to PM sources such as high-traffic roads captured more PM on their leaves than those farther from PM sources. In this study, in-wax EC content decreased with increasing distance from roads, but the relationship was not significant. The probable explanation for this is that distance was measured from the sample tree to the nearest road, regardless of the size of and amount of traffic on the road, both factors that have been shown to be important (Mori *et al.* 2015, Sgrigna *et al.* 2015).

An alternative explanation is that proximity to roads is not always the most important factor affecting overall in wax EC content. For example, one sample tree (i.e., LO3942) was located within 100 m of a high truck traffic road but exhibited one of the lowest EC contents. I speculate that this is due to a vegetation barrier that includes both shrubs and trees between the tree and the road, which could capture EC. An opposite example of this pattern is displayed in sample tree PO1600, which had one of the highest average EC contents over the four months but does not have obvious nearby EC sources such as bus stops. In this case, it is possible that cars and potentially garbage trucks that routinely drive and idle underneath the tree caused the high EC content. Overall, this study contributes to the knowledge that EC retention in leaf waxes can vary depending on proximity to EC sources.

The role of Litterfall in EC Delivery to Soil

It was hypothesized that leaf litterfall would play an important role in delivering EC to the soil at the end of the growing season, either from a large amount of litter or an accumulation of EC in waxes over time, or both. During the sample months, a decrease in accumulation of in-wax EC was observed in leaves over time. This suggests that by the time leaf abscission occurs, leaves will not contain the same amount of EC as earlier in the year, with different implications for the two focal species.

Because post oaks show temporal abscission in autumn (Johnson & Risser 1974), and our study found that post oak leaves tended to retain larger quantities of EC in April and May, and smaller quantities in June and July, post oak leaves will deliver less EC to the soil by the time they reach abscission than at the beginning of the growing season. However, large litterfall fluxes will likely result in a pulse of EC in leaves during leaf abscission. Thus, post oaks exhibit high temporal variability in leaf EC flux to soil (Figure 9). In contrast to post oak trees, live oak trees act as evergreen species and tend to retain a large amount of leaves throughout the year (Goldman 2016). Their monthly leaf litterfall fluxes are small and their monthly in-wax EC retention also decreases over time but the magnitude of that decrease is less pronounced compared to post oaks (Figure 8, Figure 9). This indicates that live oak trees will display a low and continuous flux of leaf EC to the soil.

It is apparent that litterfall fluxes vary over time. Post oaks delivered more EC in litterfall to the ground over the sampling period than live oaks (2754.72 µg /m^2/month and 621.61 µg/m^2/month, respectively, Figure 9). Post oaks display a pulse of EC in leaves to the ground at the beginning and end of the growing seasons, and live oaks contribute a fairly steady amount of EC to the ground in litterfall throughout the year

Post oak litterfall contributes more EC to the soil than that of live oaks, but occurs in seasonal pulses. Throughout the sampling period, live oaks delivered a steady amount of litterfall to the ground. Although their in-wax EC content was relatively low compared to post oaks, they likely have the potential to deliver EC almost year-round to the ground. It is also likely that a small but steady decomposition of litterfall will allow for EC incorporation into the soil, as opposed to the EC entering runoff. Further research is important to understand the fate of EC that is delivered to the ground in litterfall, including potential runoff or incorporation into soil.

CHAPTER 3

CONTRIBUTIONS TO THE FIELD OF GEOGRAPHY

This study examined EC quantities in the epicuticular waxes of two species of trees found not only in North Texas, but widespread across the southern and eastern United States. The research found significant species differences in the quantities of EC retained in tree leaves; temporal variability in EC accumulation rate; and spatial variability in EC content resulting from differences in proximity to EC sources. It also found temporal and species variability in litterfall and EC in litterfall flux to the soil.

Studies on PM removal from the atmosphere, especially the more dangerous $PM_{2.5}$, are becoming more prevalent due to the need to mitigate causes of climate change and human health hazards. Recently, biogeographers, environmental scientists, and biologists have all produced research on the topic of the potential for trees and vegetation to mitigate PM pollution (Beckett *et al.* 2000a, Chen *et al.* 2017, Dzierżanowski *et al.* 2011, Nowak & Crane 2002, Nowak *et al.* 2006). This thesis focuses on arguably one of the more harmful components of PM, and also utilizes an experimental measurement procedure to quantify EC, as opposed to estimating EC deposition through modeling. Additionally, this study presents litterfall and leaf EC litterfall measurements for individual urban trees. Few such studies have been conducted to date.

Urban Forestry and Ecosystem Services

This study contributes to a growing body of literature that demonstrates that urban trees are able to capture and retain air pollutants, providing an ecosystem service, and representing a potential form of mitigation for an especially harmful component of PM. Ecosystem services are often defined as the benefits an ecosystem can provide to contribute to human welfare (Costanza *et al.* 1997), such as riparian buffers for stream quality, or residential parks for human enjoyment. In the case of urban forestry, recent research in environmental science and geography has shown that trees in urban areas can mitigate air pollution stemming from urbanization (Bolund & Hunhammar 1999, Dobbs et al. 2011, Escobedo & Nowak 2009, Jim & Chen 2009, McPherson et al. 1998). However, many of these studies tend to be modeled, and lack experimental data.

This study contributes to the understanding of litterfall from two species of urban oak trees, and to potential pollutant removal through litterfall. No published studies have quantified litterfall from post or live oak trees in the state of Texas. Further, many litterfall studies have been conducted either a forest or controlled setting, as opposed to on individual, experimental, urban trees (Johnson & Risser 1974, Kavvadias *et al.* 2001, Lodge *et al.* 1991, Perala & Alban 1982, Saenger & Snedaker 1993, Veneklaas 2009, Vitousek 1984, Williams-Linera & Tolome 1996). The majority of studies on litterfall have measured nutrient delivery to the soil in litterfall (Lodge et al. 1991, Perala & Alban 1982, Veneklaas 2009, Vitousek 1984), but one study estimates EC in litterfall (Hara *et al.* 2014). With information on both the quantities of litterfall from urban trees, and the ability of these trees to capture EC and retain it in their leaf litter, cities may be able to better understand the dynamics of urban forestry as an ecosystem service.

Landscape and Urban Planning

Because this study has implications for urban forestry as an ecosystem service, it is important for urban planners to understand the ideal tree type and placement for pollution capture. This study found that post oak leaves captured significantly more EC than live oak leaves, which could potentially be due to the observed greater amount of wax or observed greater amount of trichomes on post oak leaves than live oak leaves.

Urban planners may benefit from this information when choosing which species to plant or conserve for effective particle capture by taking into account the amount of wax and density of trichomes on their leaves. This study shows that post oaks are significantly more efficient at capturing EC than live oaks during the months of April, May, June, and July. This proves to be an advantage, because post oaks are the third most common tree species in the City of Denton, while live oak is not in the top 10 most common (State of Denton Urban Forest 2016). However, post oaks lose their leaves in the fall, and thus are no longer able to capture particles. Therefore, although live oaks capture less EC than post oaks, it may be beneficial to plant more live oaks to continue EC removal from the atmosphere in months when post oaks do not have their leaves. The winter months are also the months when atmospheric EC concentrations are highest (Barrett & Sheesley 2014). Additionally, this finding may have implications for future investigations into a more efficient EC-capturing evergreen species than live oak that can survive in the North Texas climate. This study also shows that it is important to preserve the current post oaks and avoid development that requires their removal.

With regard to tree placement, this study provides insight on the most effective locations to place trees for EC capture. Trees closer to EC sources such as bus stops and large intersections generally had more EC in their leaf waxes than trees in residential park areas. Although it is important to keep trees in parks for aesthetic reasons, this study indicates that it is even more important to keep trees in developed areas to encourage EC capture. This study speculates that the size and amount of traffic on a road is more important than the distance a tree is from a road due to the finding that "distance from nearest road" was not a significant indicator of EC content.

Policy Recommendations

Considering the findings of this study that suggest post oaks capture significantly more EC than live oaks in their waxes, but live oaks capture year-round, these are effective policy recommendations for the City of Denton:

- Efforts to conserve post oak trees during development should be implemented, as they are effective at capturing EC.
- Live oak trees should be planted whenever possible, as they will continue to keep their leaves throughout winter, in turn capturing EC year-round.
- Particular attention to conservation of post oak trees should be focused near EC sources such as bus stops and large intersections, as should the planting of more live oak trees.

Conclusion

This study is relevant to the field of environmental geography for its spatial and human-related components, as well as to environmental science for its understanding and quantification of a harmful air pollutant. It is also in the realm of urban forestry, as it addresses the productivity of a native and non-native tree species in the North Texas area, as well as their ability to capture EC from the atmosphere based on their leaf structures. As urbanization increases, particularly in the North Texas area, it is important to study the ways in which increasing pollution can be combated for human and environmental purposes.

This study found significant differences in the quantities of in-wax EC captured by post oak and live oak trees in the City of Denton, providing pollutant removal information on two widespread tree species. It also determined that trees near sources of EC, such as bus stops and major intersections, tended to display more EC in their waxes than those farther from EC sources, such as those in residential parks. The dynamics of litterfall flux to soil for the two species were also studied, finding that live oaks delivered more litterfall to the ground in April, May, and June than post oaks, but that post oaks delivered more EC to the ground in all four months than live oaks. This study shows that biogeography plays a role in the importance of planting and placement of urban trees for efficient particulate removal from the atmosphere, and provides information that may be important to utilize in future urban planning designs.

Table 1. A list of abbreviations and their meanings

Term	Abbreviation	Definition
Abscission	N/A	Shedding of leaves from canopy
Boundary layer	N/A	A microclimate-like area of air that surrounds each individual leaf of a tree canopy, determining the ease of gaseous and particulate transport from the atmosphere to leaf surfaces
Fugitive dust	N/A	Dust generated from the mechanical disturbance of earth surface materials (e.g. construction operations, vehicles on unpaved roads)
Leaf Area Index	LAI	Measurement of the one sided green leaf area of a canopy (m^2) per unit ground surface area (m^2), dimensionless
Leaf flush	N/A	Production of new leaves by a tree, usually seasonally driven
Orographic precipitation	N/A	Precipitation caused by the lifting of moist air, formation of clouds, and deposition of rain on one side of a mountainous area
Particulate matter	PM	Organic or inorganic particles suspended in the atmosphere; PM_{10} are particles 10 microns in diameter or smaller, $PM_{2.5}$ are particles 2.5 microns or smaller (fine PM)
Radiative forcing	RF	Change in energy in the atmosphere due to climate changing gasses and particles – is positive when incoming energy exceeds outgoing energy; also called climate forcing
Volatile organic compounds	VOCs	Organic compounds that volatilize easily and form ground-level ozone when combined with nitrogen oxides

Table 2. A brief summary of recent publications involving experimental methods to understand the capture of particulate matter by vegetation

Study	Sampling Approach	Species Sampled	Location
Beckett *et al.* 2000	Deionized (DI) water rinse of full, small trees, one wash per tree, analyzed PM content	*Cupressocyparis leylandi, Pinus nigra var.maritima, Sorbus intermedia, Acer campestre, Populus deltoides X trichocarpa*	Wind tunnel
Brantley *et al.* 2014	Sampled PM & BC in roadside trees for efficiency in vegetative roadside barriers	Tree vegetation, not specified	Side of 6-lane highway, Detroit, MI
Dzierżanowski *et al.* 2011	Leaf harvest from same part of tree, DI water rinse filtered w/ sieve, repeated w/ chloroform for PM	*Acer campestre L., Fraxinus excelsior L., Platanus X hispanica Mill., Tilia cordata Mill., Forsythia X intermedia Zabel, Hedera helix L., Physocarpus opulifolius(L.) Maxim., Spiraea japonica L.*	City center, Warsaw, Poland
Hara *et al.* 2014	Leaf harvest from multiple heights, washed with DI and chloroform, BC quantified, flux of BC in litterfall calculated	*Quercus serrata, Camellia japonica*	Urban forest, Japan
Hofman *et al.* 2014	Sample for PM at multiple tree heights and azimuthal directions	*Planatus X acerifolia*	Urban street canopy, Antwerp, Belgium
Huang *et al.* 2015	Wind tunnel experiment for ultrafine PM on trees	*Ilex cornuta, Quercus alba, Magnolia grandiflora, Lonicera fragrantissima*	Wind tunnel
Levia *et al.* 2013	Quantified and modeled PM diameter distributions of bulk precipitation, throughfall, stemflow, and organic layer solution	*Fagus sylvatica L.*	Thuringia, Germany
Mori *et al.* 2015	Sampled needles for capacity to accumulate PM on the leaf surface and in waxes	*Picea sitchensis and Pinus sylvestris L.*	Busy roadway in Stavanger, Norway
Popek *et al.* 2013	Compared capacity to capture of PM from atmosphere	6 shrub species, 7 tree species	Central Poland

(table continues)

Study	Sampling Approach	Species Sampled	Location
Przybysz *et al.* 2014	Compared capacity of evergreen species to accumulate PM and trace elements from ambient air in urban areas	*Taxus baccata L, Pinus sylvestris L., Hedera helix L.*	Multiple different locations, two near roads and one in a rural setting
Reinap *et al.* 2009	Wind-tunnel based methods for plants exposed to sea-salt aerosols	*Quercus robur L.*	Wind tunnel
Saebø *et al.* 2012	Measured PM accumulation on leaves	25 shrub species, 22 tree species	Urban areas in Poland and Norway
Sgringa *et al.* 2014	PM to leaves was quantitatively analyzed in four districts of city	*Quercus ilex*	Terni, Italy

Table 3. Sample ID, dbh (cm), height (m), and LAI (m^2/m^2) of each post oak (PO) and live oak (LO) tree sampled for elemental carbon in the City of Denton, Texas

ID	Latitude, Longitude	Species	dbh (cm)	Height (m)	LAI (m^2/m^2)
PO0100	33.2305, -97.1320	Post oak	62.8	13.1	1.88
PO0225	33.2137, -97.1482	Post oak	43.5	12.9	1.77
PO0308	33.2169, -97.1516	Post oak	63.1	16.0	2.07
PO1514	33.2285, -97.1255	Post oak	48.9	14.3	1.91
PO1600	33.1982, -97.1549	Post oak	46.0	10.6	3.23
PO2100	33.2063, -97.1559	Post oak	59.7	11.2	1.96
PO2330	33.2362, -97.1344	Post oak	80.2	15.2	2.43
PO2403	33.2209, -97.1592	Post oak	44.5	10.4	3.56
PO2602	33.2387, -97.1142	Post oak	76.8	11.2	2.75
PO3201	33.2446, -97.1321	Post oak	88.0	13.0	2.82
LO0225	33.2136, -97.1482	Live oak	44.0	11.7	2.31
LO0301	33.2167, -97.1493	Live oak	46.3	11.3	4.20
LO0321	33.2179, -97.1280	Live oak	32.0	10.2	2.77
LO0712	33.2207, -97.1595	Live oak	74.6	11.9	2.91
LO1201	33.2245, -97.1229	Live oak	32.2	9.2	3.80
LO1600	33.1982, -97.1552	Live oak	79.0	16.5	3.24
LO2602	33.2379, -97.1141	Live oak	56.8	13.0	3.12
LO3020	33.2441, -97.1315	Live oak	51.0	11.8	4.03
LO3021	33.2436, -97.1317	Live oak	72.4	9.0	4.75
LO3242	33.2566, -97.1523	Live oak	50.6	10.7	2.82

Table 4. Distance from road and distance between trees sampled for paired post oak (PO) and live oak (LO) trees. Pairs greater than 200 m apart from each other are not considered to be co-located. When two distances, each distance is respective to first or second tree ID.

Pair	IDs in Pair	Distance from Road (m)	Distance between Trees (m)	Potential Nearby Sources of EC
1	PO0225, LO0225	10	10	Bus stop
2	PO1600, LO1600	10, 20	40	Traffic stop, road
3	PO0308, LO0301	10	160	Traffic stops, roads
4	PO1514, LO1201	10	450	Truck delivery area
5	PO0100, LO0321	10	800	Major traffic stop, road
6	PO2602, LO2602	20	100	Small roads
7	PO2403, LO0712	20	50	Small roads
8	PO2100, LO3942	10, 50	3500	Highway traffic/Parking lot
9	PO2330, LO3021	10	600	Traffic stops, roads
10	PO3201, LO3020	10	6	Major traffic stop, roads

Table 5. Plausible EC sources within 100 meters of each tree sampled for in-wax EC content in the City of Denton, Texas, from April to July 2017

ID	Co-located	Species	Avg. EC Retention (µg/m^2)	Plausible Nearby Sources (within 100 m)
PO0100	No	Post oak	587.76 ± 248.91	Bus stop, large intersection
PO0225	Yes	Post oak	3099.40 ± 3182.80	Bus stop, small intersection
PO0308	Yes	Post oak	534.94 ± 226.13	Small intersection
PO1514	No	Post oak	606.61 ± 209.48	Delivery area
PO1600	Yes	Post oak	1256.81 ± 7287.82	Stop sign, tree hangs over road
PO2100	No	Post oak	1136.67 ± 676.60	Freeway
PO2330	No	Post oak	762.36 ± 1287.08	Tree hangs over road
PO2403	Yes	Post oak	354.97 ± 186.82	Small roads
PO2602	Yes	Post oak	384.35 ± 220.88	Stop sign
PO3201	Yes	Post oak	1235.89 ± 6565.60	Bus stop, large intersection
LO0225	Yes	Live oak	436.38 ± 2851.04	Bus stop, small intersection
LO0301	Yes	Live oak	108.54 ± 48.25	Small intersection
LO0321	No	Live oak	160.21 ± 58.25	Bus stop, intersection
LO0712	Yes	Live oak	113.37 ± 28.28	Small roads
LO1201	No	Live oak	224.69 ± 120.45	Delivery area
LO1600	No	Live oak	115.60 ± 59.96	Stop sign
LO2602	Yes	Live oak	186.14 ± 93.73	Stop sign
LO3020	Yes	Live oak	107.40 ± 23.45	Bus stop, large intersection
LO3021	No	Live oak	161.08 ± 111.51	Bus stop
LO3942	No	Live oak	72.50 ± 30.78	Parking lot, roadway

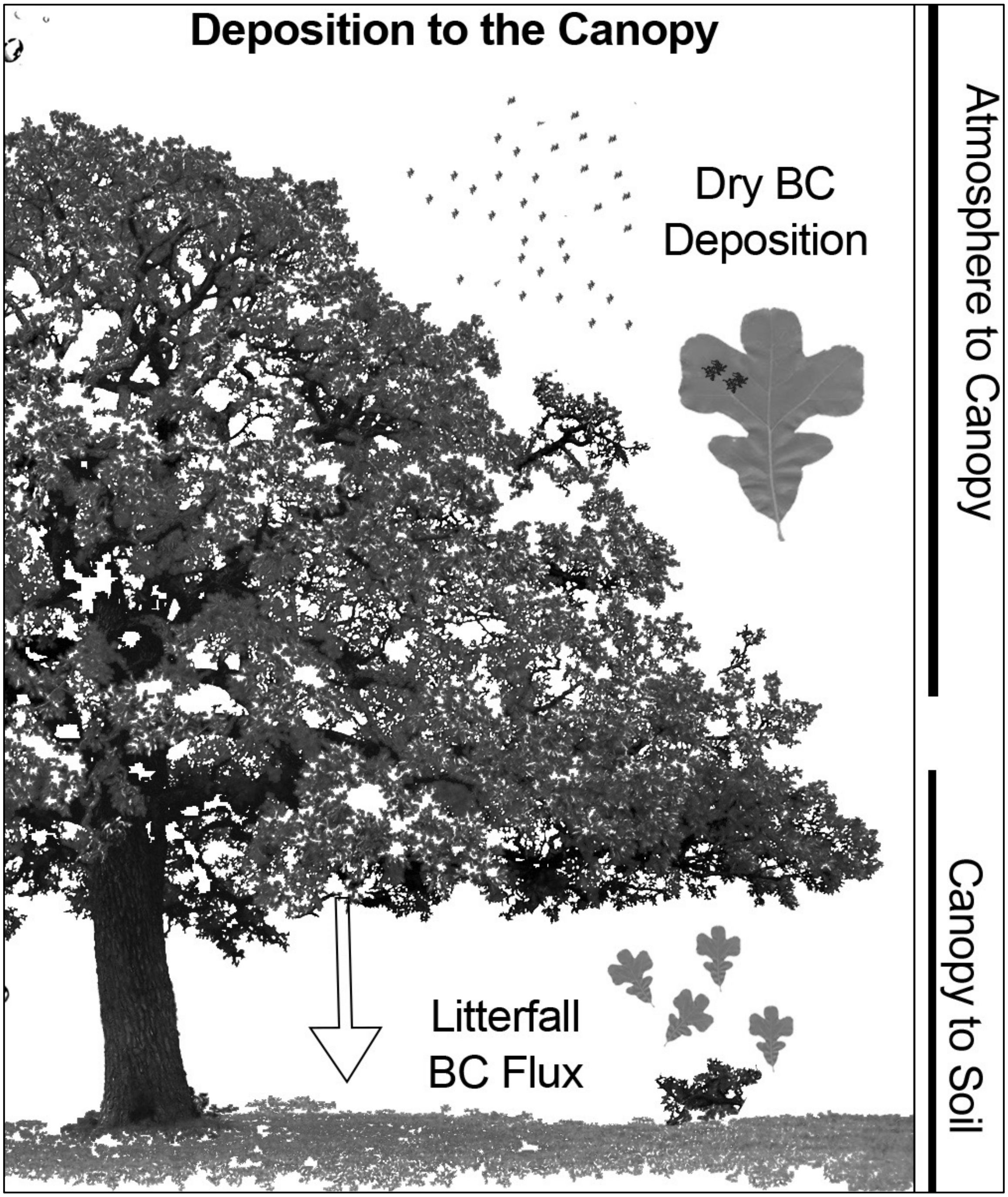
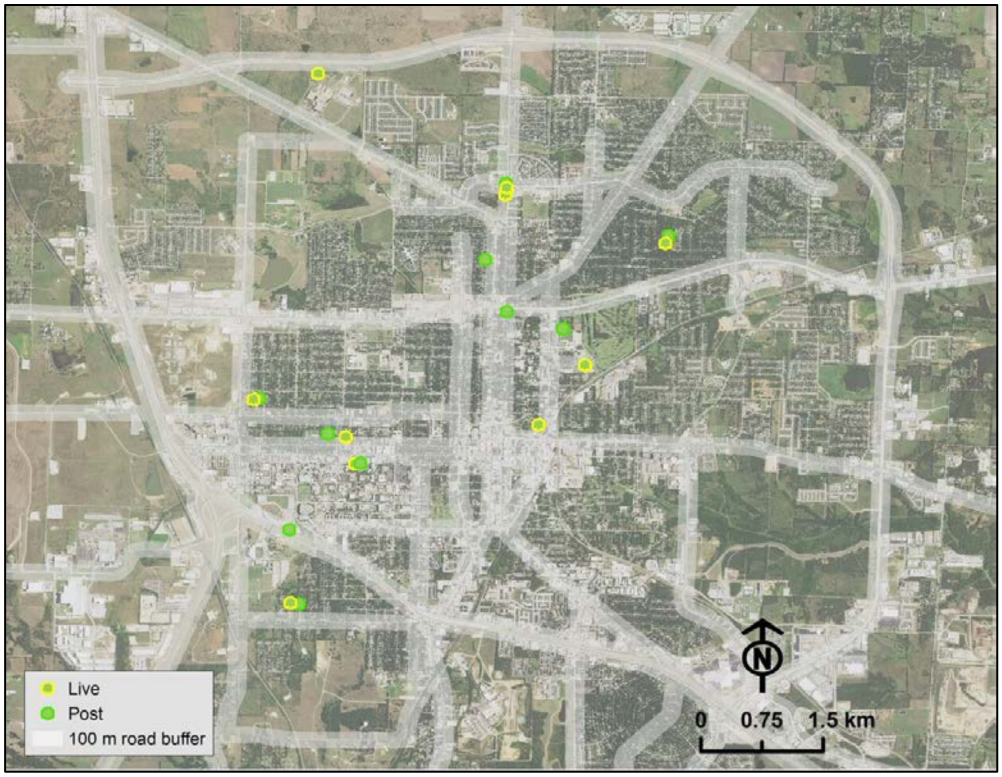


Figure 1. Mechanism of dry deposition in conjunction with litterfall: Dry atmospheric particles land on or are embedded in leaf waxes, and eventually fall to the ground in leaf litterfall.

(a) Foliar sampling locations



(b) Litterfall sampling locations

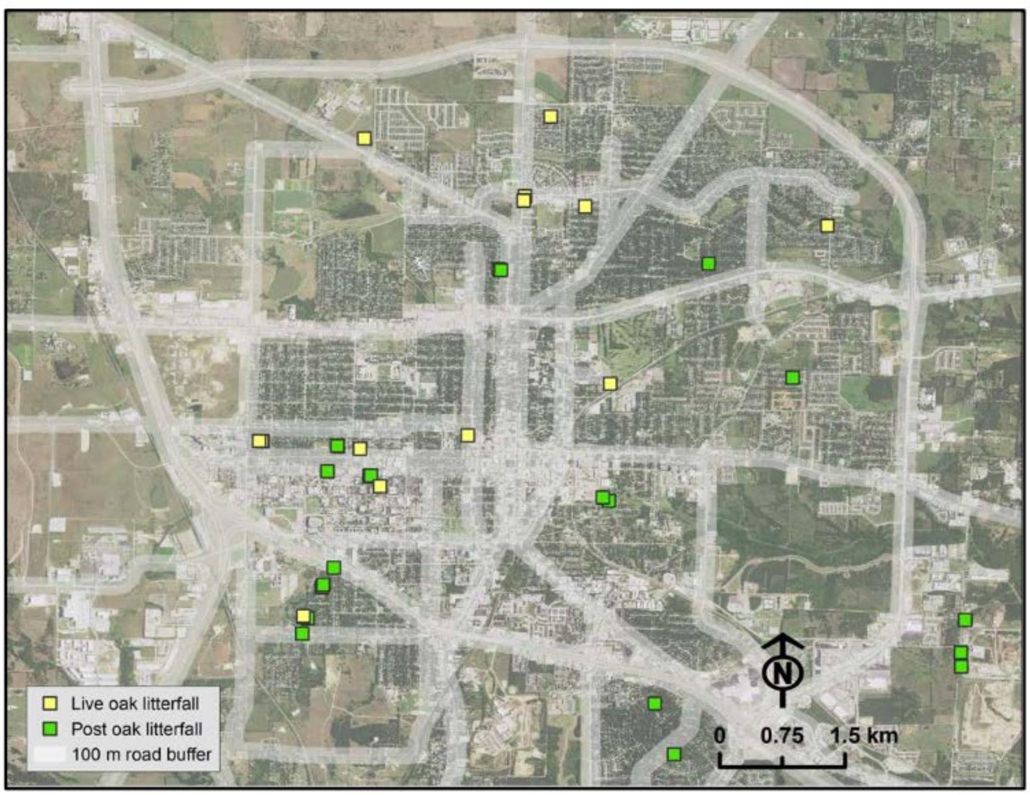


Figure 2. Map of sampling locations across the City of Denton. Ten post oak and ten live oak trees were sampled for in-wax EC content near (≤ 100 m) and far (>100 m) from roads with truck traffic from April through July 2017.

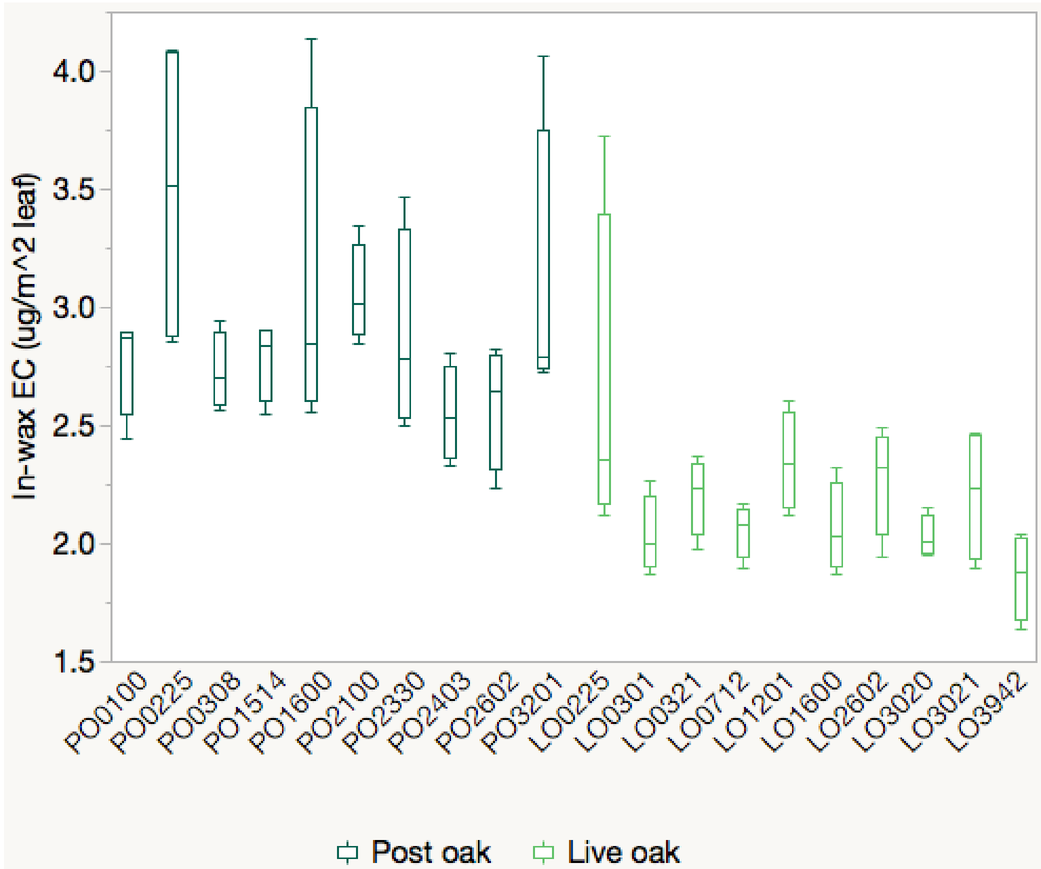


Figure 3. In-wax EC retention by tree ID. Figure shows the geometric mean of each tree over the four sampling periods (April to July 2017). For viewing purposes, data are displayed on a log scale, and error bars are standard errors.

Figure 4. Figure showing consecutive differences between chloroform extracts of PO0225 and LO0225, trees located within 10 m of each other on the University of North Texas campus in the City of Denton. This figure shows that the post oak (top row) leaves have a denser accumulation of particles and therefore darker filters than the live oak leaf (bottom row) leaves.

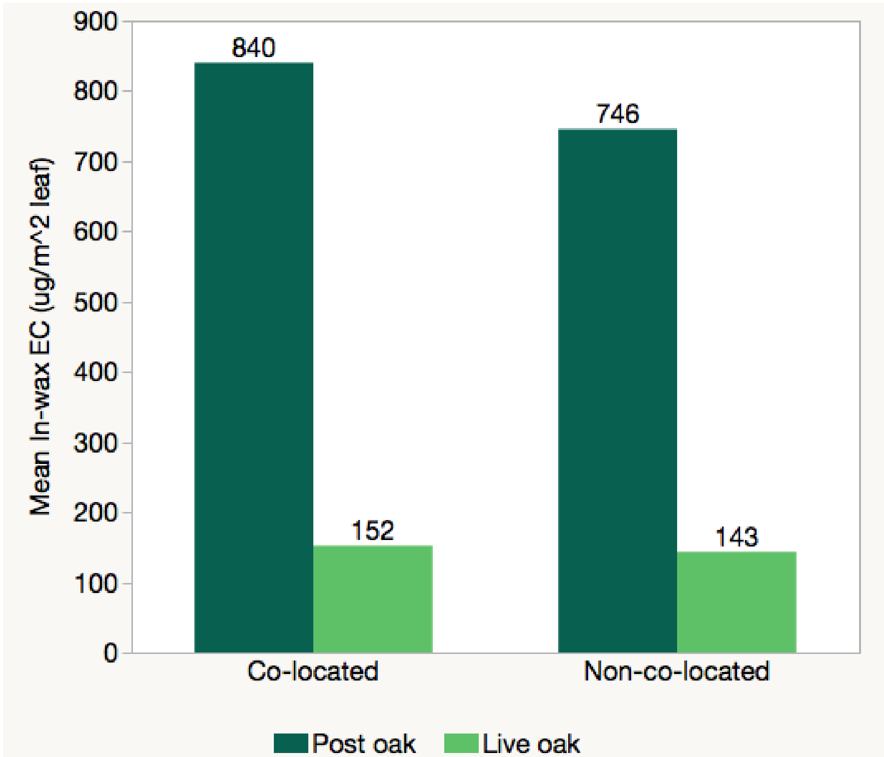


Figure 5. Geometric mean of in-wax EC (μg/m²) for post and live oak trees at co- and non-co-located sites. Trees were sampled from April to July 2017 in the City of Denton, Texas.

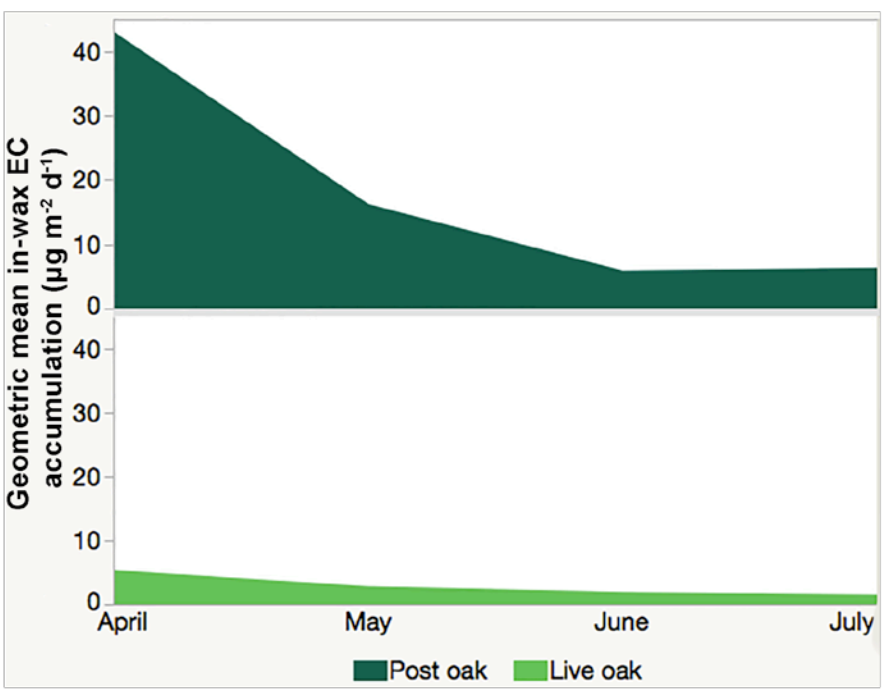


Figure 6. Net in-wax leaf EC accumulation for post oaks and live oaks sampled in the City of Denton, Texas, over the sampling period from April to July 2017.

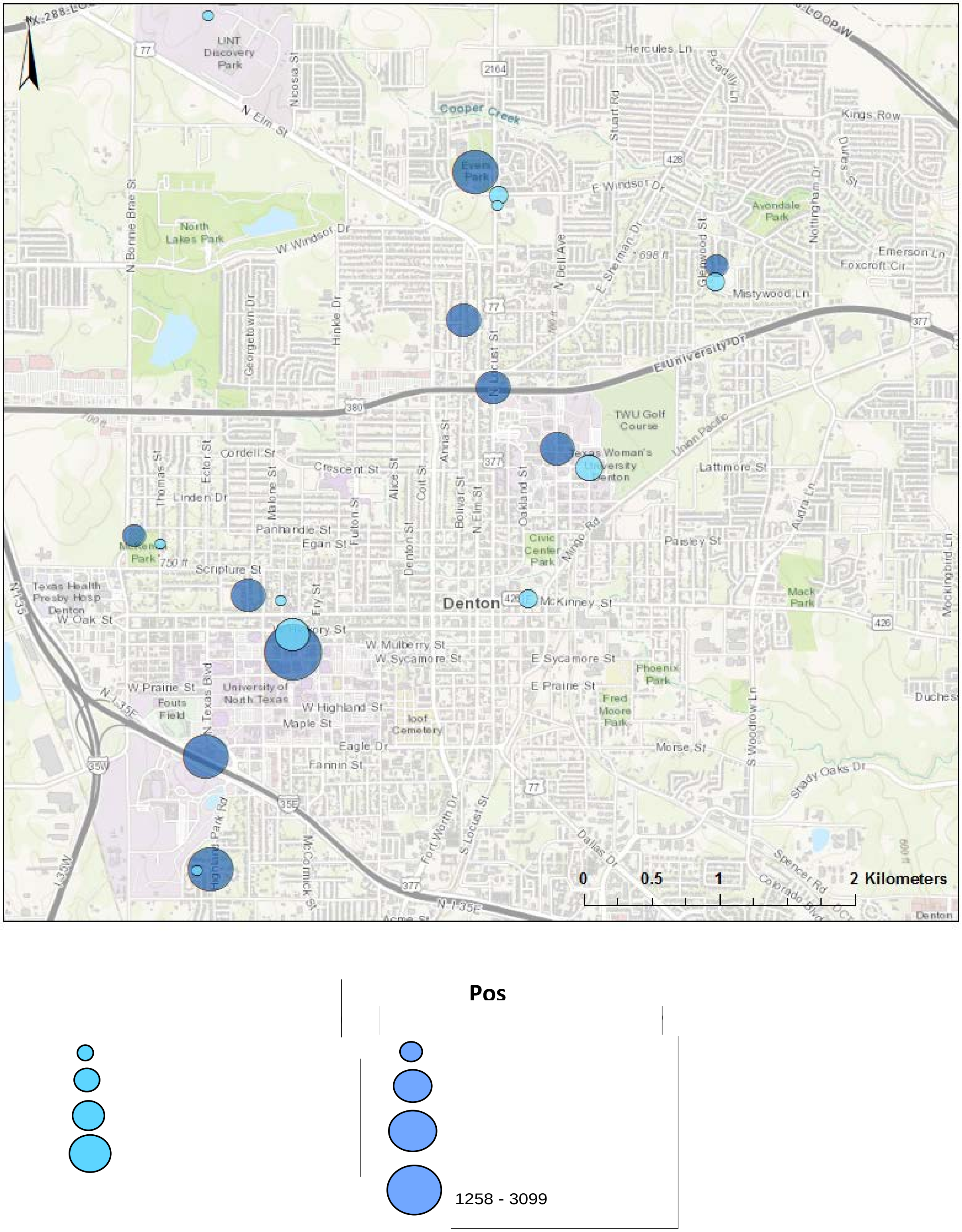


Figure 7. Map of sampling sites, including their geometric mean EC content per tree over the four sampling periods (April to July 2017).

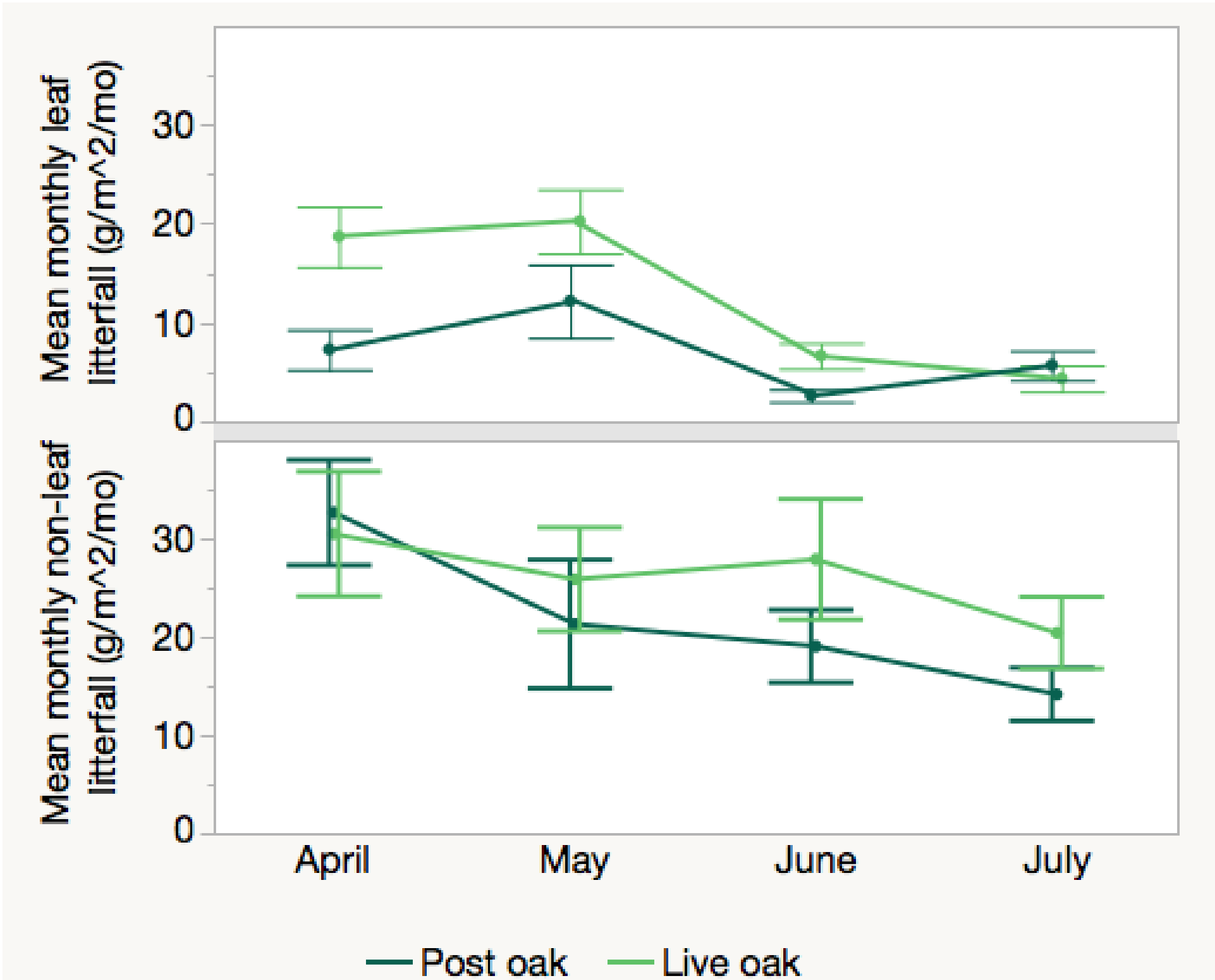


Figure 8. Arithmetic mean of monthly leaf and non-leaf litterfall for post and live oak trees. Each point represents the mean flux of litterfall (SE) to the ground for each species during the sample months from April through July 2017 in the City of Denton, Texas. Error bars are standard errors.

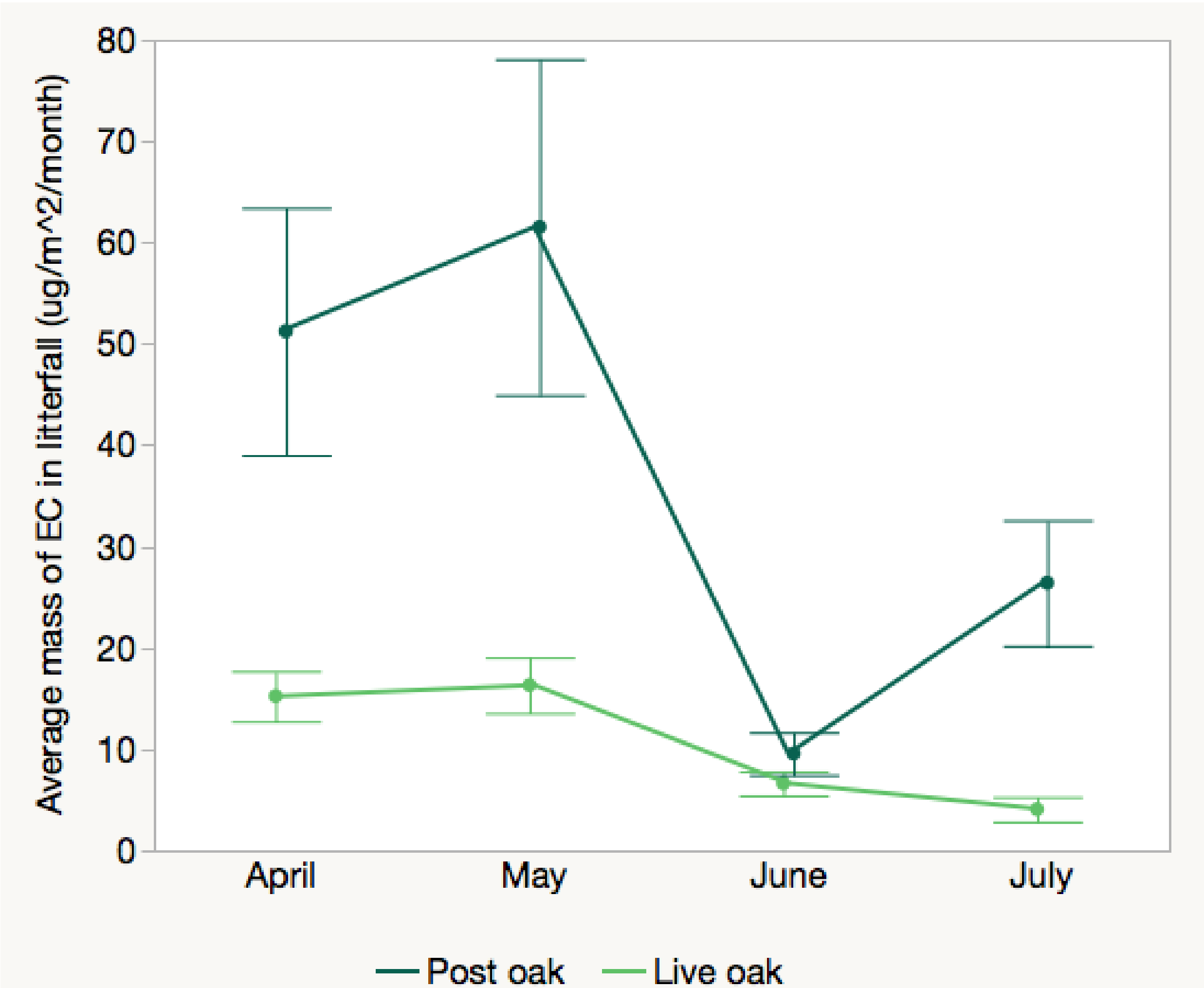


Figure 9. Arithmetic mean of monthly in-wax EC in leaf litterfall for post and live oak trees. Each point represents the mean flux of EC in leaf litterfall (SE) to the ground for each species during the sample months from April through July 2017 in the City of Denton, Texas. Error bars are standard errors.

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